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PROGRESS IN RESEARCH AND DEVELOPMENT ACTIVITIES ON MOLTEN CARBONATE CARBONATE FUEL CELLS AT CECRI, KARAIKUDI*

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The progress made in the development of Molten Carbonate Fuel Cells (MCFC) at CECRI has been reviewed. Porous nickel electrodes were prepared by loose powder sintering, slurry casting and tape casting techniques. Nickel - 10% Cr was used as the anode. The nickel electrodes lithiated under in-situ conditions served as the cathode. Electrolyte structure was fabricated by tape casting technique. Single cells were tested at a cell voltage of 0.65 V delivering a total current of 7.2 A (165 mA/cm^2).

Keywords: Molten carbonate fuel cells, electrodes and tape casting.

INTRODUCTION

Molten Carbonate Fuel Cell (MCFC) is expected as one of the most attractive electric power plants in the future, because it can directly generate electric power at high energy conversion efficiency [1,2]. One application will be small dispersed generators using gaseous fuel from natural gas upto few kW level. The other would be as central power plants using gasified coal as fuel for onsite power generation (mega-watt level).

Molten Carbonate Fuel Cells (MCFC) are capable of delivering the D.C. electricity by the electrochemical reaction between any hydrogen rich carbonaceous fuel and oxygen at 923 K. The cell reaction occurs on two electrodes sandwiched on both sides of a tile containing molten carbonate as the electrolyte. The electrode reactions, materials employed have been described earlier [3,4].

MCFC programme at CECRI, Karaikudi

The research and development programme on MCFC has been started at CECRI in 1992. This programme exclusively aims at high level of technological research in which electrochemistry and materials technology play an important role. The focus points attempted in the above programme are

* Establish reliable fabrication technologies for the state of art materials and characterise them.
* Design and fabrication of cell components and testing them under laboratory cell conditions.
* Evaluation of new materials for the electrodes and electrolyte structures.
* Under the above programme the results achieved and the progress made were periodically reported [5,6].
* The current programme of the MCFC development at CECRI is sponsored by the Ministry of Nonconventional Energy Sources (MNES), New Delhi. The objective of the project is demonstration of MCFC monocell with 1000 cm^2 geometric area electrodes with a capacity of 100 watts.
* The progress made in this direction is reported in this paper.

EXPERIMENTAL

Component development

Preparation of matrix material (γ-$LiAlO_2$)

The details of the preparation of the matrix material powder (γ-$LiAlO_2$) by various methods has been reported earlier [6]. The material has been characterised by JEOL X-RAY Diffractometer (MODEL JSM - 8030). A new proprietary technique for the synthesis of γ-$LiAlO_2$ called combustion synthesis was developed using various fuels like urea, glycine and different sources of Li salts as reported elsewhere [7]. The particle size distribution and surface area measurements were also carried out. It was possible to prepare γ-$LiAlO_2$ powder with uniform particle size distribution (10.1-7.9 μm) with varying surface area (10-50 m^2/g). Synthesis of $LaAlO_3$ and $LaGaO_3$ was also carried out by solid state reaction and combustion synthesis method for use as alternate matrix materials.

TABLE I: Quality control tests for electrodes and matrix materials

Test	Property
Powder (γ-$LiAlO_2$)	
Density	Bulk, Tap and Absolute density
Particle size analysis	Particle size distribution
SEM	Powder morphology
BET analysis	Surface area
XRD	Phase composition
Green electrodes, electrolyte and matrix tapes	
Density measurement	Green density values
Visual observation	Bubbles, inclusions and other defects
Dimension measurements	Thickness and thickness ratios shrinkage after casting and curing
Optical microscopy	Defects during formation and bonding
TGA	Organic content removal and weight loss during heating
Sintered samples	Sintering parameters
Density measurement	Sinter density values
Porosity measurement	Open porosity (vol %)
Dimension measurement	Thickness and sintering shrinkage
Mercury porosimetry	Pore size distribution and porosity
SEM	Microstructure and bonding

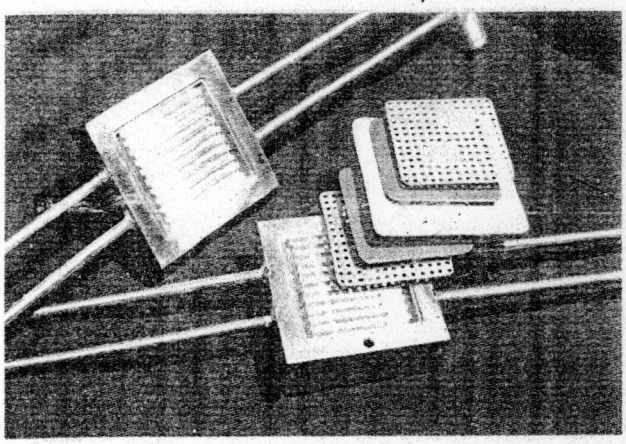

Fig. 1: Photograph showing the assembly components

Preparation of electrolyte matrix structures

Usually, an eutectic mixture of Li_2CO_3 and K_2CO_3 (62:32 mole ratio) is employed as the electrolyte. A porous tile of γ-$LiAlO_2$ is used as the matrix to hold the electrolyte. The nominal composition of matrix to electrolyte powder varies in the ratio 40:60 wt.% to 45:55 wt.% respectively. Tape casting was employed as the method to prepare thin (0.5 - 1.0 mm) tapes of electrolyte, matrix and electrolyte + matrix structures. A slurry formulation was prepared with PVA as the binder in aqueous medium (for matrix tapes only) and poly vinyl butyral as the binder using non-aqueous solvents. The details of the procedure are proprietary [8]. The matrix structures were subjected to various characterisation tests as described in Table I.

Preparation of electrodes

Ni powder (INCO 255) was used to prepare the electrodes. Several batches of electrodes were prepared by loose powder sintering and tape casting method. Ni powder + 10 wt.% Cr powder (75 - 90 μm) was used to prepare the anode. The cathode was usually a Ni electrode oxidised and litaiated insitu inside the cell. Pre lithiated NiO powder was also used to prepare the electrodes. The electrodes were also subjected to various characterisation tests as described in Table I.

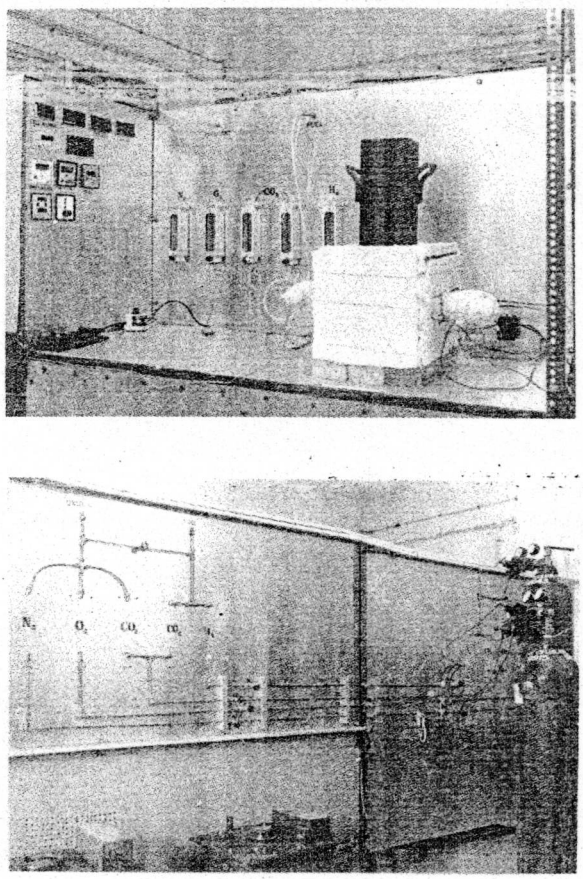

Fig. 2: Photograph showing the fuel cell test bench front and rear view

The cell assembly component fabrication

The cell assembly used for the present investigation is different from the design reported earlier [3]. The present design incorporates testing of electrodes of square size. Two sets of end plates with SS 316L were fabricated. Electrodes of two different sizes 6.7 x 6.7 (45 cm^2) and 12.5 x 12.5 (150 cm^2) can be accommodated in them. The end plates had provisions for gas inlet by an external manifolding device and the gases pass through the straight grooves to the gas collector manifold on the opposite end. The groove width and depth were optimized by trial and experimentation. The electrodes rest on the ribs over a current collector (1.0 mm thick) of Ni perforated sheet on the anode side and SS perforated sheet on the cathode side. The matrix and electrolyte tapes rest on the full area of the end plates and held in position between the anode and cathode. The two end plates were arranged in such a fashion that the direction of the gas flow was in coflow mode. The entire assembly of the components is shown in the photograph (Fig. 1).

The cell assembly was packed and kept inside a furnace assembly and thermally protected. A specially designed test bench has been created incorporating gas flowmeter, gas manifolding pipes, temperature controller cum indicators and voltmeters for comprehensive evaluation studies. The test set up is shown in the photograph (Fig. 2). Two cells can be tested simultaneously in the above set up. The reactant gases at the inlet manifolds were preheated to above 423 K. The cell was started at a slow heating rate of 274 K per minute and maintained at different intermediate stages for different durations upto 773 K. Initially the cells were started with N_2 and CO_2 on both the chambers and after the cell attains

TABLE II: Characteristics of cells tested

Cell no	Electrode area (cm^2)	Anode	Cathode	OCV (V)	Current (A)	Current density (mA/cm^2)	Cell voltage (V)	Hrs of testing
2	45	CC	TC	0.909	2.156	48	0.67	96
6	45	Ni-Cr(CC)	TC	0.800	1.209	27	0.54	110
10	45	TC	TC(IOL)	0.942	1.320	30	0.54	120
12	45	TC	TC(IOL)	0.911	1.751	40	0.72	132
14	45	Ni-Cr(CC)	TC(PO)	0.935	7.400	164	0.62	375
18	45	TC	TC	0.970	2.770	61	0.63	528
20	45	Ni-Cr(CC)	TC(IOL)	0.891	1.634	37	0.63	120
22	45	Ni-Cr(CC)	TC(EO)	0.953	7.620	170	0.63	700
30	150	Ni-Cr(CC)	TC(IOL)	0.950	7.200	72	0.63	200

*CC - Cold compacted and sintered; *TC - Tape cast and sintered; *IOL - Insitu oxidised and lithiated
*PO - Pre oxidised; *EO - Exsitu oxidised

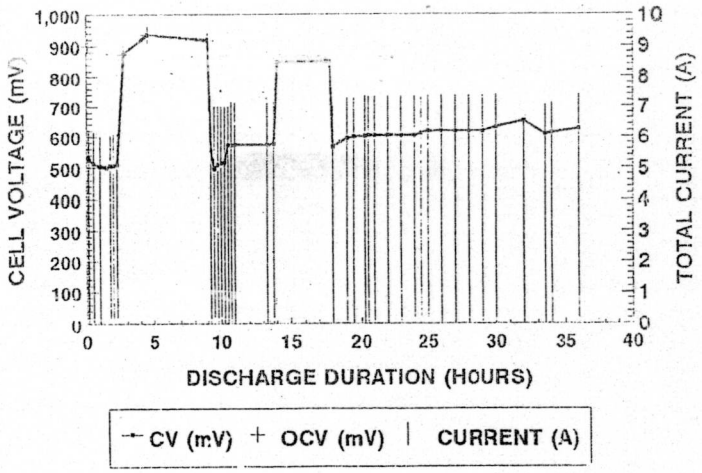

Fig. 3: Discharge curve for cell no 14 after 300 hours at 923 K

773 K the reactant gases were switched over to the following nominal compositions.

Anode gas

H_2 80 vol% + CO_2 20 vol% (80 - 200 ml/min) minimum and (400 - 600 ml/min) maximum

Cathode gas

O_2 37 vol% + CO_2 63 vol% (50 - 100 ml/min) minimum and (200 - 300 ml/min) maximum

The sequence of heating rates and gas compositions are reported separately [9]. The cells were further heated upto 923 K at the same heating rate when the electrolyte eutectic mixture melts and fills up the pores in the matrix and diffuses to certain extent into the two electrodes. During this process the cathode gets oxidised and lithiated insitu. The filling up of the anode boundary layer forms the bubble barrier layer. At this stage the cell slowly attains the reversibly open circuit voltage close to a value above 975 mV.

Nearly 27 cells have been tested. The nature of the electrode and matrix material employed and the characteristics of the cells are given in Table II. The low open circuit voltage of the cells were ascribed to the difficulties encountered in the supply of feed gases at uniform flow rates and to the corrosion of materials. The wet seal area was not protected from the carbonate coming out from the matrix at 923 K. This problem is being looked into by developing suitable insulator coating methods. This voltage of the cell numbers 14 and 22 for different durations of test hours are indicated in Figs. 3 and 4 respectively. The cell number 14 with 45 cm^2 area electrodes, attained an OCV of 0.820 V after 100 hours of start and finally reached a value of 0.935 V after 300 hours. During this period the cell was also subjected to a thermal fluctuation between 923 and 673 K. After 300 hours the cell 14 was discharged intermittently and continuously for about 40 hours. The maximum discharge current was 7.4 A (164 mA/cm^2) at the cell voltage 0.62 V, while the minimum was 2.0 A (44 mA/cm^2) at 0.687 V. The vertical lines in Fig. 3

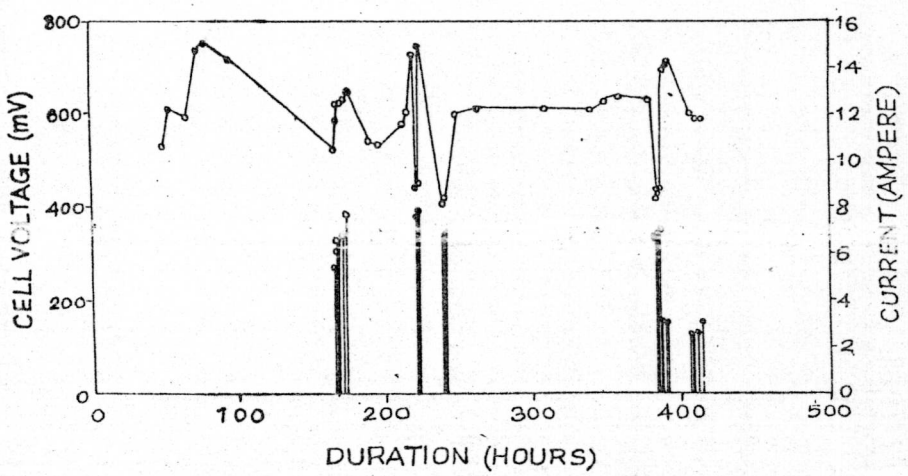

Fig. 4: Discharge curve for cell no 22

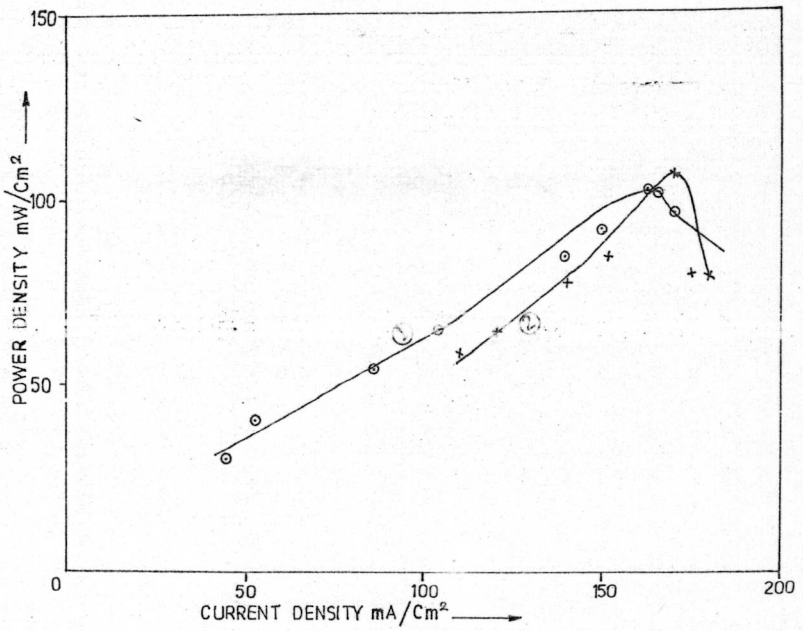

Fig. 5: Power density - current density relation for cells 14 (1) and 22 (2)

indicate the magnitude of the discharge current. During intermittent discharge, the cell voltage reaches back to the OCV when the load becomes zero.

Similarly, the Fig. 4 also represents the voltage cell characteristics of cell number 22 with 45 cm^2 area components. The characteristics are very similar to cell number 14. This cell has also been subjected to thermal cycling between 923 and 623 K. The maximum OCV of 0.80 V was attained. This cell was also discharged at high currents 7.62 A (169 mA/cm^2) at a cell voltage of 0.633 V. The minimum load was 5.12 A (113 mA/cm^2) at a cell voltage of 0.51 V. Both the above two cells exhibited an increase in the cell voltage during discharge at constant current continuously and reverted to the OCV when the load was removed.

TABLE III: The design targets under the present programme

Characteristics	Stage 1	Stage 2
Electrode area (cm2)	150.0	1000
Open circuit voltage (V)	0.975	0.975
Single cell voltage (V)	0.7-0.75	0.65-0.70
Output current (A)	15.0-18.0	120-150
Current density($mA.cm^{-2}$)	100-120	120-150
Single cell output (Watts)	10	100
Life expectancy (h)	100	1000
Number of cells in the stack	2-5	5-10
Stack voltage (V)	1.5-3.5	3.5-7.0
Stack output	20-60	500-1000

The power density - current density curves for the above two cells are indicated in Fig. 5. The above figure indicates that the maximum power density realized correspond to 103 mW/cm^2 for cell no. 14 and 109 mW/cm^2 for cell no. 22. This value is very much close to the values (105 mW/cm^2 i.e., 0.70 V at 150 mA/cm^2 to 120 mW/cm^2 i.e. at 0.75 V at 160 mA/cm^2) reported by the various international developers of MCFC [10]. The Table II also indicates the performance data of cells with 100 cm^2 area where the maximum attainable current density was found to be in the range 40 to 80 mA/cm^2 only. Efforts are underway to improve the performance of these cells close to the value reported earlier by proper design and optimization of the parameters like gas distribution, gas flow rate and electrolyte content which may influence the cell performance.

Future programme of work

The present stage of MCFC developments aims at the demonstration of 10 watts capacity MCFC monocells having an electrode area of 150 cm^2 with an expected output of 10 watts per cell. This will be accomplished by proper optimization to achieve current density values of the order of 150 mA/cm^2 as reported for cells with 45 cm^2 area electrodes. Subsequently the cell size will be increased to 1000 cm^2 with an expected output of 100 watts per cell. The tasks under this proposed programme are indicated in Table III. The final aim is to demonstrate a 500 watts capacity multicell stack.

It is envisaged that during this course, problems relating to fabrication of bipolar plate, stacking, gas distribution and sealing will be addressed. The expertise gained will be used to scale up the stack size in the range 1 to 5 kW and build up experience in stack engineering, system design and system management. The ultimate goal is the design and fabrication of 10 kW MCFC with internal reforming action suitable for natural gas. This will enable CECRI to go in stream with the international programme.

CONCLUSION

A steady progress has been made in the demonstration of molten carbonate fuel cells of 100 cm^2 size at CECRI during the past four years. The performance level of these cells are in comparison with the values (105 - 110 mW/cm^2) reported by others. These investigations are indicative of our capabilities in building and demonstration of a 100 watts capacity MCFC with 1000 cm^2 area which will be the basis for future development and demonstration of a 5 kW MCFC stack.

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